

ing, electron density map and listing of refined parameters have been deposited.

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Synchrotron X-ray Study of the Electron Density in α -Al₂O₃

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Abstract

Structure factors for corundum, α -Al₂O₃, have been measured using 0.7 and 0.9 Å synchrotron radiation as well as Mo *K*α ($\lambda = 0.71069$ Å) radiation. The stronger structure factors from two sets of synchrotron data and three sets of Mo *K*α tube data for two small crystals are remarkably consistent. In analysing those data, extinction corrections evaluated by minimizing differences between equivalent reflection intensities were compared with those from the more common procedure of least-squares determination of the extinction parameters as a part of the structure refinement. Difference electron densities evaluated with extinction corrections from equivalent reflection intensities are more consistent than those which optimize $|F_o|$ versus $|F_c|$ agreement. Approximate symmetry in the concordant densities is related more closely to the Al—Al geometry than to nearest neighbour Al—O interactions. Space group *R*3*c*, hexagonal, $M_r = 101.96$, $a = 4.7540$ (5), $c =$

12.9820 (6) Å, $V = 254.09$ (6) Å³, $Z = 6$, $D_x = 3.997$ Mg m⁻³, $\mu(0.9 \text{ Å}) = 2.361$, $\mu(0.7 \text{ Å}) = 1.097$, $\mu(\text{Mo } K\alpha) = 1.139$ mm⁻¹, $F(000) = 300$, $T = 293$ K, $R = 0.024$, $wR = 0.030$, $S = 4.84$ for the unique 0.7 Å synchrotron reflection data.

Introduction

The corundum α -Al₂O₃ structure can be classified as an archetypal special class within the important perovskite *ABX*₃ series. The series as a whole includes many compounds with a wide variety of physical properties. Even the metal sesquioxides with the α -Al₂O₃ structure have some markedly different properties. A detailed understanding of the structure and electron density for the parent α -Al₂O₃ compound is a prerequisite to classifying physical property/structure relationships for the perovskite series as a whole.

Over the past decade the electron density in single crystals of α -Al₂O₃ has been measured in X-ray diffraction analyses by Lewis, Schwarzenbach & Flack (1982), Tsirelson, Antipin, Gerr, Ozerov &

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Struchkov (1985), Aslanov (1989) and Kirfel & Eichhorn (1990), referred to below as LSF, TAGOS, A and KE, respectively, using a range of experimental techniques and crystal specimens.

Three 152 μm diameter crystals for the A and TAGOS studies from the same source (E. J. Gabe, National Research Council of Canada at the XII International Congress of Crystallography held at Ottawa in 1981) were studied using Mo $K\alpha$ radiation data analysed with a conventional independent-atom model for the structure. The deformation electron density in α -Al₂O₃ was analysed in terms of Hirshfeld-type deformation functions, using Mo $K\alpha$ structure factors for a 200 μm diameter crystal and Ag $K\alpha$ structure factors for a 130 μm diameter crystal, by LSF. Recent work by KE was partly directed to refining a deformation density multipole model for a 200 μm diameter corundum crystal using synchrotron radiation with wavelength 0.5599 (1) Å.

Those experimental studies of the electron-density distribution have been complemented by extensive *ab initio* theoretical calculations. In a calculation within an HF-LCAO framework, Salasco, Dovesi, Orlando, Causa' & Saunders (1991) used the program CRYSTAL88 (Dovesi, Pisani, Roetti, Causa' & Saunders, 1989). A multipole scattering X_α (MSX $_\alpha$) approach, which is essentially a density-functional method, was applied to α -Al₂O₃ by Nagel (1985). There is a band-structure calculation by Ciraci & Batra (1983).

While these investigations have much in common, there are significant discrepancies between the deformation-density maps reported, in spite of the high accuracy claimed for the structure-factor measurements in each experiment. There are equally large discrepancies between the authors' interpretations of their maps. This motivated us to carry out further independent studies, aimed at identifying the source of the discrepancies between the published analyses.

Maslen & Spadaccini (1993) identify problems that may originate in the common practice of determining extinction corrections as part of structure refinement by least-squares minimizing of differences between observed and calculated structure factors. It has become almost standard practice to evaluate variable parameters in the extinction correction formulae for real crystals proposed by Zachariasen (1967) and by Becker & Coppens (1974*a,b*). Extinction correction by least-squares procedures can be justified provided the analysis of the measurements satisfies conditions on which the least-squares principle depends for its validity. Those conditions are specified in the Gauss-Markov theorem (*e.g.* Prince, 1982): the most probable parameters will minimize the weighted sum of squares of components if their contributions to the residual are independent, and distributed normally with unit variance.

Comparison of the extinction corrections for published studies of the electron density in α -Al₂O₃ with values determined for much smaller crystals by Streltsov & Maslen (1992) showed that the corrections did not have the crystal size and wavelength dependence expected of extinction. It appears that serious uncertainties in supposedly accurate studies of α -Al₂O₃ are likely when attempting to correct experimental data for extinction by comparing observed and calculated structure factors *a posteriori*.

Extinction corrections from standard least-squares refinements depend on the structure-factor model employed. They are sensitive to the weights of the observations to a degree that precludes accurate results. When parameters in an extinction model are determined by minimizing differences between observed and calculated structure factors, the least-squares residual is dominated by a limited number of strong low-angle reflections. High statistical uncertainty as a result of limited numbers may be compounded by systematic error if these same reflections are strongly affected by the redistribution of electron density as a result of bonding.

Deficiencies in a structure-factor model may interact with the determination of the extinction corrections in a least-squares process. This is particularly obvious when the electron-density distribution in a crystal is modelled by a superposition of spherical atoms, commonly known as the independent-atom model. However difficulties persist even when more flexible local multipole expansions for the electron densities are utilized. When assessing the reliability of multipole-expansion models it is necessary to consider the extent to which adjustments to the multipole coefficients compensate for errors in the extinction corrections. High statistical correlation may cause least-squares minimization of a residual to be ill-conditioned if extinction parameters and multipole coefficients are determined simultaneously. Such cases are readily identified because small adjustments to the weights of the observations alter the extinction corrections drastically.

Zachariasen (1967) showed that for microcrystals with maximum dimensions less than 1 μm , kinematic conditions of diffraction are necessarily fulfilled. The diffraction from larger specimens approaches this limit asymptotically as the crystal size is reduced, at a rate dependent on the size and distribution function for the perfect crystal microdomains, of which the real crystal is composed.

We may therefore use small crystals in an effort to reduce the effects of secondary extinction, and thus to improve the accuracy of strong low-order structure factors which are important for deformation electron-density studies. The high intensity of synchrotron radiation permits the study of crystals that are sufficiently small for diffraction to be nearly

kinematic (Bachman, Kohler, Schulz & Weber, 1985), while providing adequate precision in the measurements of the weaker structure factors.

An alternative approach for estimating extinction corrections applicable to small crystals that does not rely on theoretical models of the structure factors has been proposed by Maslen & Spadaccini (1993). This approach has been successfully applied to extinction evaluation for electron-density studies in calcite and magnesite crystals (Maslen, Streltsov & Streltsova, 1993*a,b*), which have the same space group, $R\bar{3}c$, as corundum. Differences between intensities for equivalent reflections with different path lengths are minimized by least-squares optimization of variable parameters in an extinction formula (Larson, 1970). This technique eliminates the dependence of the extinction corrections on the structure-factor model when those corrections are determined as part of the structure refinement. The number of relevant observations is also larger than that for refining a structure using symmetry-unique observations. The increased sample size improves the statistical precision of the determination. An additional check on the extinction corrections may be provided by the ratios of intensities in data sets measured at different wavelengths.

Experimental

In order to check previous results, several sets of diffraction data for small crystals of this compound were measured using Mo $K\alpha$ radiation and synchrotron radiation at wavelengths 0.7 and 0.9 Å. Two specimens with natural faces selected for X-ray diffraction were prepared by flux growth methods. The crystals were distorted octahedra exhibiting two {021}, two {0 $\bar{1}$ 1}, two { $\bar{1}$ 11} and two {101} faces for crystal 1, and two {003}, two {0 $\bar{1}$ 1}, two { $\bar{1}$ 11} and two {101} faces for crystal 2, with dimensions 20 × 38 × 38 μm, respectively, for crystal 1 and 20 × 44 × 44 μm for crystal 2. The crystal dimensions were measured and the faces indexed using optical and scanning electron Philips SEM505 microscopes. The crystals were mounted with the short axis approximately horizontal to increase the spread in path lengths required for the extinction corrections.

Diffraction data set 1 was measured with crystal 1 mounted on a Syntex $P2_1$ four-circle diffractometer. Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation from the X-ray tube was monochromated by an oriented graphite monochromator in the equatorial setting. Crystal 1 data sets 2 and 3 were measured with synchrotron radiation at wavelengths 0.6991 (1) and 0.9000 (1) Å using the BL14A four-circle diffractometer (Satow & Iitaka, 1989) at the Tsukuba Photon Factory.

Vertically polarized synchrotron beams were monochromated with two Si(111) crystals, using a curved mirror to focus the X-rays. By positioning the specimen slightly off-focus, changes to the synchrotron radiation intensity as a result of instabilities in the particle beam were minimized. Mo $K\alpha$ data sets 4 and 5 were measured for crystal 2. Experimental details are set out in Table 1.

Lattice constants were determined from 15 2θ values for data set 1 ($50 < 2\theta < 53^\circ$), for data sets 4 and 5 ($33 < 2\theta < 38^\circ$), 12 2θ values for data set 2 ($36 < 2\theta < 58^\circ$) and eight 2θ values for data set 3 ($77 < 2\theta < 98^\circ$). Reflection intensities were measured systematically for the complete sphere of reciprocal space with $(\sin\theta/\lambda)_{\max} = 1.08 \text{ \AA}^{-1}$, $-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-27 \leq l \leq 27$ for data set 1 and with $(\sin\theta/\lambda)_{\max} = 1.0 \text{ \AA}^{-1}$, $-9 \leq h \leq 9$, $-9 \leq k \leq 9$, $-24 \leq l \leq 24$ for data sets 2, 3, 4 and 5. $\omega/2\theta$ scans were used for all data sets. The stronger intensities for 0.9 Å data set 3 were reduced by an absorber with an attenuation factor of 34.09. Six standard reflections were monitored every 100 reflections to check the stability of the incident beam. The measured intensities were modified for fluctuation of the standards and the variances adjusted as suggested by Rees (1977). The variances in measured structure factors from counting statistics were modified for source instability as indicated by the standards and increased when necessary by comparing intensities of equivalent reflections following a Fisher test. Reflections having measured variances consistent with Poisson statistics were assigned the Poisson variance. Variances for other reflections were adjusted according to the scatter of equivalents.

The correction for thermal diffuse scattering (TDS) was estimated with a modified version of the program *TDS2* by Stevens (1974). The elastic constants for corundum were from Landolt-Bornstein (1966). The TDS corrections, having a maximum value of 1.0044, were negligible. Linear absorption coefficients μ at Mo $K\alpha$, 0.7 and 0.9 Å, were evaluated from atomic absorption coefficients by Creagh (1992). Lorentz and polarization corrections were applied and absorption corrections (Alcock, 1974) evaluated analytically. All calculations utilized the *Xtal3.2* crystallographic programs (Hall, Flack & Stewart, 1992) implemented on SUN SPARC and DEC 5000/120 workstations. Further experimental and refinement details are given in Table 1.

The effects of counter deadtime on the synchrotron radiation intensities were corrected by determining coefficients in a truncated series expansion in powers of the deadtime (Satow, 1992). The NaI counter deadtime was measured to be 1.2 μs. The 0.7 Å data set 2 for crystal 1 with an R_{int} value low in comparison with the Mo $K\alpha$ data sets in Table 1 appears to be accurate. Part of the reduction in R_{int}

Table 1. *Experimental and refinement data for α -Al₂O₃*

	Crystal 1			Crystal 2	
	Data set 1	Data set 2	Data set 3	Data set 4	Data set 5
Radiation	Mo K α	Synchrotron	Synchrotron	Mo K α	Mo K α
λ (Å)	0.71069	0.6991 (1)	0.9000 (1)	0.71069	0.71069
Diffractometer	Syntex P2 ₁	PF†	PF†	Syntex P2 ₁	Syntex P2 ₁
Monochromator	Graphite	Si(111)	Si(111)	Graphite	Graphite
Scan speed (° min ⁻¹)	5.86	16	16	5.86	5.86
Peak scan width ($a + b \tan \theta$)	0.7; 0.8	0.25; 0.0	0.2; 0.16	0.7; 0.8	0.7; 0.8
Max. 2θ (°)	100	90	130	90	90
Max. intensity variation of standards (%)	$\pm(012)$ $\pm(024)$ $\pm(234)$ 2.8	$\pm(\bar{1}64)$ $\pm(6\bar{3}4)$ $\pm(154)$ 4	$\pm(606)$ $\pm(666)$ $\pm(0\bar{6}6)$ 7	$\pm(\bar{1}\bar{1}2)$ $\pm(113)$ $\pm(\bar{3}00)$ 2.5	$\pm(\bar{1}\bar{1}2)$ $\pm(113)$ $\pm(\bar{3}00)$ 5.3
No. of observed reflections [$> 1\sigma(I)$]	2198	2600	2491	2037	1998
Transmission range	0.942	0.944	0.885	0.956	0.956
	0.977	0.977	0.958	0.979	0.979
No. of independent reflections	214	249	249	204	209
Extinction, † r^*	247 (215)	634 (186)	-4213 (151)	834 (442)	582 (438)
Min. extinction, $\mu\text{\S}$	0.99	0.98	1.00	0.98	0.99
$R_{\text{int}}(F^2)$, before	0.053	0.030	0.024	0.049	0.050
after absorption	0.052	0.030	0.027	0.048	0.049
extinction applied	0.052	0.030	0.027	0.048	0.049
R	0.026	0.024	0.032	0.025	0.026
wR	0.033	0.030	0.026	0.031	0.026
S	3.41	4.84	9.22	3.33	2.70
Max. shift/e.s.d.	0.00007	0.00019	0.00025	0.00015	0.00036
Extinction, † refined r^*	4780 (366)	13016 (662)	10556 (987)	5173 (517)	10913 (1043)
Min. extinction, $\mu\text{\S}$	0.89	0.85	0.82	0.92	0.86
R	0.021	0.015	0.014	0.020	0.018
wR	0.023	0.017	0.019	0.021	0.020
S	2.41	2.72	6.75	2.33	2.05
Max. shift/e.s.d.	0.00006	0.00028	0.00714	0.00061	0.00075

† The BL14A four-circle diffractometer (Satow & Iitaka, 1989) at the Tsukuba Photon Factory, Japan.

‡ Maslen & Spadaccini (1993) approach.

§ $F_{\text{obs}} = yF_{\text{kin}}$, where F_{kin} is the value of the kinematic structure factor.

¶ Zachariasen (1967) extinction corrections included in least-squares structure refinement (Larson, 1970).

is as a result of improved counting statistics resulting from higher beam intensity.

F_o extinction corrections were determined for the full data sets by the method of Maslen & Spadaccini (1993) before structural parameters were determined. It should be noted that strong reflections for the 0.9 Å synchrotron data set would be affected more strongly by any errors in the counter deadtime or expansion coefficients. If some reflections within a group of equivalents were affected by counter dead-time errors more strongly than the remainder, the erroneous corrections would interact with any real variation between equivalent reflection intensities due to extinction. This may explain why the absorption correction increased the R_{int} factor and why a negative 'extinction' parameter was obtained for the 0.9 Å data set 3.

The reference state for structure-factor calculations was the independent-atom model. Those structure factors were evaluated using spherical atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), with dispersion corrections $\Delta f'$, $\Delta f''$ of 0.065, 0.052 at Mo K α , 0.064, 0.050 at 0.7 Å and 0.098, 0.084 at 0.9 Å for Al; and 0.012, 0.006 at Mo K α , 0.011, 0.006 at 0.7 Å and 0.018, 0.010 at 0.9 Å for O, evaluated by Creagh (1992). For each data set nine independent parameters, including anisotropic vibration tensor elements, were determined by full-matrix least-squares refinement based on $|F|$ with least-squares

weights equal to $1/\sigma^2(F_o)$ for all measured structure factors. Details are given in Table 2.† An isotropic extinction parameter, r^* (Larson, 1970), was evaluated during each structure refinement for comparison with those from the method of Maslen & Spadaccini (1993).

Structural parameters

The Al atom in α -Al₂O₃ is located on the threefold axis at 0,0, z , with the O atom at $x,0,\frac{1}{4}$ in the hexagonal setting of $R\bar{3}c$. The structural parameters from all refinements (Table 2) agree well, with maximum deviations of 1 e.s.d. for z (Al), 2 e.s.d.'s for x (O) and 4 e.s.d.'s for the temperature factors. The refined parameters from the more accurate synchrotron data set 2 are in close agreement with the refinement of synchrotron data by Kirfel & Eichhorn (1990), being within 2 e.s.d.'s for all parameters.

† Lists of structure factors for all five data sets and figures of deformation-density sections in the (01 $\bar{1}$ 0) plane through O and two Al atoms for data sets 1, 3, 4, 5 and 3 scaled on data set 2 with the extinction corrections evaluated by minimizing differences between equivalent reflection intensities and with the extinction parameter included in the structure refinement have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71271 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0628]

Table 2. Fractional coordinates and anisotropic vibration parameters for α -Al₂O₃

	Crystal 1			Crystal 2		
	Data set 1	Data set 2	Data set 3	Data set 4	Data set 5	
<i>z</i> (Al)	0.35222 (6)	0.35223 (4)	0.35221 (2)	0.35227 (5)	0.35228 (4)	
<i>x</i> (O)	0.69424 (28)	0.69378 (17)	0.69376 (9)	0.69396 (24)	0.69401 (19)	
<i>U</i> ₁₁ (Al)	0.00236 (17)	0.00206 (12)	0.00252 (9)	0.00217 (16)	0.00234 (13)	
<i>U</i> ₃₃ (Al)	0.00265 (24)	0.00252 (17)	0.00242 (12)	0.00221 (24)	0.00230 (20)	
<i>U</i> ₁₁ (O)	0.00282 (36)	0.00247 (20)	0.00276 (12)	0.00255 (32)	0.00253 (25)	
<i>U</i> ₂₂ (O)	0.00274 (47)	0.00258 (26)	0.00303 (13)	0.00296 (42)	0.00281 (34)	
<i>U</i> ₃₃ (O)	0.00270 (43)	0.00278 (25)	0.00281 (15)	0.00212 (40)	0.00274 (34)	
<i>U</i> ₁₃ (O)	0.00029 (19)	0.00028 (10)	0.00032 (5)	0.00025 (17)	0.00032 (14)	

The O-atom geometry in the corundum structure can be regarded as approximating hexagonal close packing, with Al atoms occupying two thirds of the trigonally distorted octahedral interstices. Each Al atom is surrounded by six O atoms. Three of these lie at the corners of an equilateral triangle 1.327 Å above the central Al, with a shortest O—O contact of 2.5215 (10) Å. Each of these O atoms participates in an Al—O bond of length 1.9700 (2) Å. The remaining three form another equilateral triangle 0.837 Å below the central Al atom, staggered with respect to the one above, with an O—O vector length of 2.8629 (12) Å. Each O atom in the second triangle is bound to Al by a strong Al—O bond of length 1.8525 (5) Å. Each O atom is surrounded by four Al atoms, two at 1.8525 (5) and two at 1.9700 (2) Å from the Al.

Each Al atom has ten Al near neighbours in the α -Al₂O₃ structure. The Al—Al vector along the threefold axis across the face shared by two AlO₆ coordination octahedra of 2.6544 (7) Å has the shortest Al—Al distance in the structure. The other three near-neighbour Al—Al vectors are 2.7882 (2) Å across the edges shared by AlO₆ octahedra in the basal plane. These Al—Al distances in α -Al₂O₃ are short in comparison with the Al—Al distance of 2.864 Å in crystalline Al metal. The consequences for the electron density are discussed below. The next six shortest Al—Al vectors, three of length 3.2144 (4) and three of length 3.4950 (5) Å, are directed across corners of the AlO₆ octahedra. The Al—Al distance along the threefold axis through the empty octahedral interstices is 3.8366 (7) Å.

Electron density

Sections of the electron-difference density, $\Delta\rho$, for the more accurate synchrotron data set 2 in the plane (01 $\bar{1}$ 0) through Al and O atoms and in the plane (0001) through O atoms are shown in Figs. 1 and 3. These are based on extinction corrections determined from equivalent reflection intensities by the method of Maslen & Spadaccini (1993). The corresponding difference-density section in the plane (01 $\bar{1}$ 0) with an extinction parameter included in the structure refinement (Larson, 1970) is depicted in Fig. 2. The 0.1 e Å⁻³ contour interval is more than twice

the value of $\sigma(\Delta\rho) = 0.04 \text{ e Å}^{-3}$ evaluated by the method of Cruickshank (1949). Sections equivalent to Figs. 1 and 2 for all other data sets are deposited.*

The difference density for the synchrotron data sets 2 and 3 is less noisy than the maps for tube data sets 1, 4 and 5. That is the expected consequence of poor counting statistics for the predominantly weak reflections measured with low-intensity tube X-ray sources for small crystals. The general topography of these $\Delta\rho$ maps overlaps that of the maps by LSF, TAGOS, A and KE sufficiently to justify confidence that the structure-factor measurements for the present and previous analyses are basically concordant. Common features are pronounced positive density near the Al-atom position, similar to that observed by TAGOS, the semi-circle region of positive density near the O atoms, and depletion of density near the Al—Al contact along the threefold axes which occurs in all maps.

At a detailed level, however, there is considerable variation between the Fig. 2 type maps for all data

* See deposition footnote.

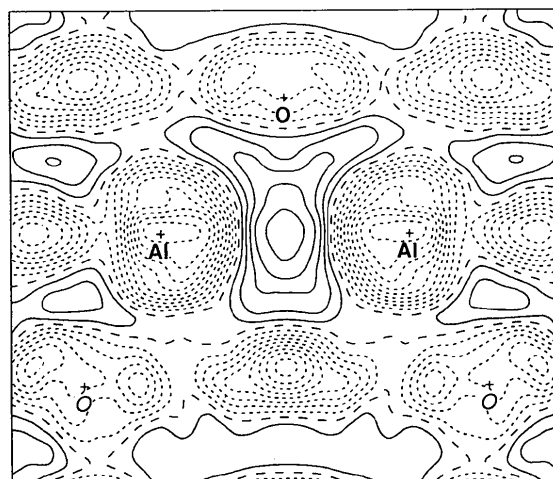


Fig. 1. $\Delta\rho$ for α -Al₂O₃ in the (01 $\bar{1}$ 0) plane through two Al and three O atoms with two O atoms deviating from the plane by 0.11 Å, shown in italics. Data set 2. Extinction corrections were evaluated by minimizing differences between equivalent reflection intensities. Map borders 5.1 by 5.9 Å. Contour interval 0.1 e Å⁻³, positive, negative contours — solid, short dashes, respectively.

sets. A dependence of extinction corrections estimated as part of the structure refinement on the weights of the observations identified by Streltsov & Maslen (1992) would explain the discrepancies between the Fig. 2 maps. A similar dependence of $\Delta\rho$ on the statistical precision of the measurements would account for the large differences between maps reported by A and TAGOS for three crystals from one source.

The Fig. 1 type difference densities, with extinction corrections evaluated from equivalents, agree with one another more closely than Fig. 2 maps, with

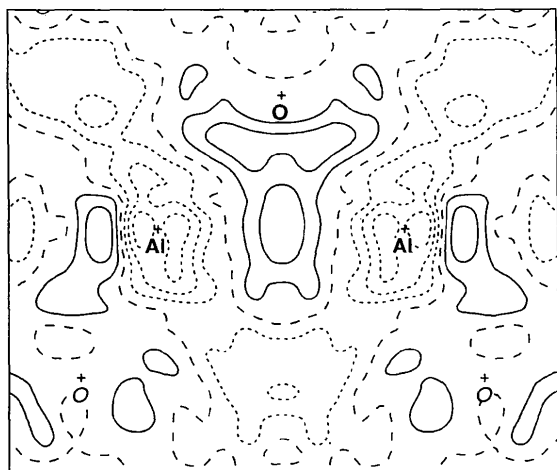


Fig. 2. $\Delta\rho$ for α -Al₂O₃ in the plane as Fig. 1. Data set 2. Extinction corrections were determined as part of the least-squares structure refinement. Map borders and contour interval as for Fig. 1.

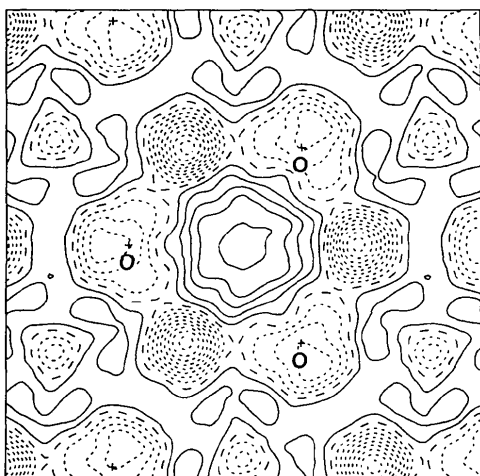


Fig. 3. $\Delta\rho$ for α -Al₂O₃ in the (0001) plane through three O atoms for data set 2. Map borders 5.1 by 5.1 Å. Extinction correction and contour interval as for Fig. 1.

extinction parameters evaluated as part of the refinement. We must conclude therefore, that either the residual extinction errors in data sets 1 to 5 are identical but large, which is unlikely since the experiments involved two different crystals and three different radiations, or that Figs. 1 and 3 are basically correct.

The symmetry of the $\Delta\rho$ map in Figs. 1 and 3 approximates sixfold, which is higher than the threefold symmetry expected from the Al—O bond geometry. At first sight this appears unreasonable. However, the higher symmetry of the maps corresponds to that of the shortest Al—Al contacts noted above. We must therefore examine the likelihood that the $\Delta\rho$ topography is predominantly determined by second-nearest neighbour Al—Al interactions. As the nearest Al—Al vectors in α -Al₂O₃ are shorter than the corresponding Al—Al vector in Al metal, the hypothesis that Al—Al interactions predominantly determines the appearance of the $\Delta\rho$ map is not unreasonable.

The equilibrium separation in Al metal can be regarded as reflecting a balance between attractive forces, generated by the attraction between the nuclei and the electrons of neighbouring atoms with the inter-nuclear and inter-electron repulsions. Exchange terms in the wavefunction increase the effective inter-nuclear repulsions by removing electron density from the inter-nuclear region when electrons with parallel spins overlap strongly. Where an Al—Al vector is shorter than the equilibrium separation in the metal, exchange depletion of the electron density, and hence the effective inter-nuclear repulsion, is increased. That is consistent with the strong depletion of the density near the Al nucleus along the Al—Al vector in the Fig. 1 map. Electrons removed by exchange depletion are forced to accumulate in regions of lower electrostatic potential. In α -Al₂O₃ there is such a region roughly midway between the Al nuclei. In Al metal those electrons accumulate in the inter-nuclear Fermi sea that is responsible for the electrical conductivity of the metal.

Atomic charges determined by projecting $\Delta\rho$ onto atomic density basis functions (Hirshfeld, 1977) are listed in Table 3. Results for the 0.7 Å synchrotron radiation and Mo *K*α data sets are consistent. Values for the 0.9 Å synchrotron data are less reliable because the data set 3 charges are strongly affected by the uncertain accuracy of strong low-angle reflections which have large deadtime corrections. Where the extinction parameter is optimized within the least-squares refinement of the structural parameters the polarity of the structure is reduced, by approximately 0.05 electrons per atom. That charge reduction is consistent with the results reported by Buttner & Maslen (1992*a,b,c*) for perovskite compounds, but the effect is smaller for α -Al₂O₃.

Table 3. *Atomic charges for α -Al₂O₃ (e)*

Radiation	Crystal 1		Crystal 2	
	Data set 1	Data set 2	Data set 4	Data set 5
Al	Mo $K\alpha$ 0.36 (2)	Synchrotron 0.7 Å 0.37 (2)	Mo $K\alpha$ 0.31 (2)	Mo $K\alpha$ 0.31 (3)
O	-0.24 (2)	-0.24 (2)	-0.21 (2)	-0.21 (2)
Al*	0.35 (2)	0.30 (2)	0.25 (2)	0.25 (3)
O*	-0.23 (2)	-0.20 (2)	-0.17 (2)	-0.17 (2)

* Zachariassen (1967) extinction corrections included in least-squares structure refinement (Larson, 1970).

Discussion

Synchrotron radiation focused with a curved mirror was preferred to a parallel 0.5 Å beam used in earlier experiments. With the specimen slightly off-focus the beam intensity at the crystal was more stable than that with the parallel beam. The high intensity of the focused longer-wavelength beams improved the statistical precision of the weaker reflections. In the case of the 0.7 Å radiation that did not impair the accuracy of the strong reflections by introducing serious uncertainties in the counter deadtime corrections, which were a problem for the 0.9 Å synchrotron data set. The remarkable consistency of the results for the synchrotron source with 0.7 Å wavelength radiation with that obtained from tube data sets for two small crystals suggests high reliability.

The shortcomings of the 0.9 Å data affect only the two strongest reflections directly. The remainder are affected indirectly *via* the scale factor determined in the least-squares refinement. An independent determination of the scale would eliminate that error for the majority of the reflections. The extinction corrections obtained from equivalent reflections, being negligible for 0.7 Å radiation, are expected to be small even at 0.9 Å. The 0.9 Å data were therefore rescaled by comparison with the 0.7 Å radiation. The corresponding difference map in the plane (01 $\bar{1}$ 0) (deposited*) is notably more consistent with the other maps than it was previously.

The difference-density maps calculated by *ab initio* theoretical calculations of the electronic structure for α -Al₂O₃ (Salasco, Dovesi, Orlando, Causa' & Saunders, 1991) and by the cluster method (Nagel, 1985) are in close agreement with previous 'experimental' maps by LSF and KE. However, although theory can properly be used to complement experimental data, care is necessary when comparing diffraction-sourced results with theoretical calculations (Mackenzie & Mathieson, 1992), especially for lattice structures.

There are no density maps for the band-structure calculations which shown low ionicity for the Al—O bonding reminiscent of the present low 'experimental' values of atomic charges. For example, from

the band-structure calculation of Ciraci & Batra (1983) the Al charge was +1. The study of Julg, Pellegatti & Marinelli (1980) by a self-consistent field method gives an Al charge of +0.57, and +0.33 was obtained from an empirical relation connecting hardness and ionicity of a crystal. On the other hand, the cluster MSX_{α} approach (Nagel, 1985) gave +2.57 and an *ab initio* calculation (Salasco, Dovesi, Orlando, Causa' & Saunders, 1991) gave +1.78.

The band-structure calculation of Ciraci & Batra (1983) demonstrated the importance of the Al—Al interaction when evaluating the actual width of the upper valence band. The conduction-band states are mainly Al-like and have a minimum at the centre of the rhombohedral Brillouin zone along the threefold axis. This shows that the fundamental gap is indirect with an energy of 8.7 eV, which agrees well with the experimental value. More extensive comparison of theory and experiment for α -Al₂O₃ is desirable.

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* See deposition footnote.

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X-ray Study of the Electron Density in Magnesite, MgCO₃

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Abstract

The electron density in a naturally faced mineral crystal of MgCO₃ was re-measured with Mo *K* α ($\lambda = 0.71073$ Å) diffraction data, using extinction corrections that minimize differences between equivalent reflection intensities. The deformation electron density has $0.66 e \text{ \AA}^{-3}$ density maxima in the C—O bonds and $0.35 e \text{ \AA}^{-3}$ maxima at the O-atom lone pairs. Space group *R* $\bar{3}c$, hexagonal, $M_r = 84.31$, $a = 4.635$ (1), $c = 15.023$ (2) Å, $V = 279.5$ (1) Å³, $Z = 6$, $D_x = 3.005 \text{ Mg m}^{-3}$, $\mu(\text{Mo } K\alpha) = 0.48 \text{ mm}^{-1}$, $F(000) = 252$, $T = 293 \text{ K}$, $R = 0.022$, $wR = 0.025$, $S = 5.87$ for 332 unique reflections.

Introduction

Carbonate minerals derive their identity from the CO₃ group which typifies coherent, non-molecular structure segments that act as rigid bodies. Analysis of the CO₃ group's rigid-body vibrations in magnesite (Finger, 1975) shows translation and libration motions parallel to and about the *c* axis, and in the plane normal to *c*. Disorder of that CO₃ group, consistent with a rigid-body riding motion was suggested by early authors, but no positional disorder in the planar CO₃ anion was observed in deformation electron-density ($\Delta\rho$) maps by Göttlicher & Vegas (1988), who explained the maps in terms of ionic interactions between Mg and CO₃ ions. The $\Delta\rho$ topography at the middle of the Ca—O vector in calcite, CaCO₃ (Maslen, Streltsov & Streltsova, 1993), is far from that often considered as typifying covalent interactions, but this contradicts the Effenberger,

Kirfel & Will (1983) interpretation of positive $\Delta\rho$ regions at the mid-points of the Ca—O and Mg—O vectors in dolomite, CaMg(CO₃)₂, in terms of covalency in those bonds.

Göttlicher & Vegas (1988) observation of an electron-density bridge between O atoms along the longest edge of the MgO₆ octahedron contrasts with lower density near a short O—O distance outside that octahedron, which in magnesite is among the shortest non-bonding O—O contacts for all calcite-type carbonates (Effenberger, Mereiter & Zemann, 1981). No similar $\Delta\rho$ increase along the longest edge of the CaO₆ octahedron occurs in calcite (Maslen, Streltsov & Streltsova, 1993). The density increased slightly between the short edge of the CaO₆ octahedron and near the mid-point of the short non-bonding contact between O atoms. Magnesite and calcite span the extreme range of lengths for this contact in the isomorphous carbonate minerals.

In most electron-density studies carried out so far, extinction was corrected by least-squares fitting of extinction parameters for structure factors from a crystal model to the observed structure factors. Those extinction parameters correlate strongly with the scale factor and some model parameters. Least-squares minimization of a residual may be so ill-conditioned that small adjustments to the weight of the observations alter the extinction correction drastically, introducing artefacts (Streltsov & Maslen, 1992).

Correlation of extinction parameters with the scale-factor and model parameters can be avoided. The extinction corrections for large magnesite slabs cut parallel to a desired face in the study by Gött-